X-764-73-224

PREPRINT

HEAT PIPE STABILITY I: A PRELIMINARY INVESTIGATION INTO THERMALLY ASSISTED CAVITATION

JULY 1973

GSFC

GODDARD SPACE FLIGHT CENTER

GREENBELT, MARYLAND

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*This report is an outgrowth of heat pipe development contract NAS5-11455.

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ABSTRACT

This paper introduces in a preliminary manner the notion of thermally assisted cavitation by localized fluctuations in capillary forces. Because cavitation in liquids can be closely approximated by an isothermal process, only momentum and mass balances are used to introduce the notion for liquids under mechanical tension. The corresponding phenomena for the electrocapillary effect is not considered. Brief attention is given to developing a stability theory in terms of the stiffness and compliance coefficients for a working fluid. Interestingly, the particular thermodynamic approach taken can be used to suggest experiments relating working fluid performance to meniscus behavior.

A correction to the liquid flow equation is suggested.

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HEAT PIPE STABILITY I: A PRELIMINARY INVESTIGATION INTO THERMALLY ASSISTED CAVITATION

INTRODUCTION

In referring to the concept of wetting, it is customary to relate the referral for a given material to a contact angle measured at room temperature. The angle so measured is therefore an equilibrium value; variations in thermodynamic forces will cause variations in this angle, but the fluctuation normally disappears when standard conditions are reestablished. Engineering calculations customarily assume a contact angle of zero in the Laplace equation because angles are usually judged small. If this assumption is justified in all cases, then the equilibrium state of the meniscus is defined for zero angle, and any departure resulting from fluctuations in thermodynamic forces causes a shift away from equilibrium with the possibility of an accompanying shift in contact angle away from zero. A contact angle of zero means simply that the adhesive forces between liquid and substrate exceeds the cohesive forces between liquid particles sufficiently to cause spreading, and the liquid to flow sufficiently to form a layer approaching the thickness of a monolayer, that is, the sine of the contact angle is zero, and the covering layer at prevailing conditions appears to the substrate as an extension itself.

Because the Laplace equation forms the basis for steady state momentum and energy transfer generated by capillary phenomena, it must also serve as a starting point for stability investigations. We commence our discussion from the first variation, viz,

$$\delta(P_g - P_L) = \frac{\delta\gamma}{R}\cos\theta - \frac{\delta R}{R^2}\gamma\cos\theta - \frac{\gamma}{R}\sin\theta\,\delta\theta \quad , \tag{1}$$

since ultimately it is the functional relationship of pressures, radii of curvature etc. with space and time coordinates, which establishes the notion of stability or lack thereof. Ideally, it is possible to transfer thermal energy isothermally because density fluctuations across an interface at the phase change temperature generates a pressure fluctuation and fluid flow. However, because of viscous effects, fluctuation dissipation occurs and interferes with energy transport. As a result, temperature gradients are normally introduced, and operation is removed from equilibrium considerations becoming subject to analytical formulation as a steady state problem. Locally, however, to speak of processes as occurring isothermally offers convenience, and is justified by treating a device such as a heat pipe as being made up of sections, and with some lack of consistency by saying also that thermal gradients are small. A gradient may be

small, but if the dependent variable is not, linearization may not be justified, particularly if the structure of stability relationships is required. After this ado, we begin by examining equation (1) for the isothermal case. Since $\delta\theta < 0$ for $\theta \to 0$, then $\delta(P_g - P_L) = O$ provided the curvature compensates such that $\delta R > O$, or at the boundary the meniscus becomes tangent. Changes have therefore occurred in a conservative manner. Keeping this conservation relationship, the isothermal requirement may be relaxed, $\delta (P_g - P_L) = \delta\gamma / R (\cos\theta)$, and over some temperature range, where $\delta\gamma$ is significant, pressure fluctuations are controlled by surface tension whereas δR is controlled by adhesion to the wall. Next, looking at the situation of fluctuations about $\theta = O$, $\delta(P_g - P_L) = O$ and the functional relationships are conservative if along some segment not attached to the boundary, the meniscus changes shape such that they are related by $\delta R > O$ then $\delta\gamma > O$ and $\Delta T < O$, or the meniscus complies by becoming more rigid by removing particles from the liquid. Reversing equality signs produces the opposite effect. In the isothermal case, pressure changes must occur for δR. For $\delta R > O$, $\delta P_L > \delta P_g$ and the density of gas over the given locale in the meniscus will increase; for $\delta R < O$ condensation occurs. As a basis for the above discussion, pinning of the meniscus at the boundary at $\theta = O$ was assumed, and therefore a film of liquid, a monolayer or so in thickness, exists along some portion of the boundary. Also at this contact angle, a gradient in heat of vaporization exists from the film to the meniscus proper.

Although the above discussion of the Laplace equation is incomplete, enough has been said to provide some basis for the elaboration of the stability problem and its relationship to the bubble formation mechanisms outlined below.

Approach

The steady state transfer of heat by a liquid under tension occurs because a differential in curvature exists between evaporation and condensation interfaces. To zeroth order, the difference is a design feature incorporated into a device such as a heat pipe. Flow velocity is as a result dependent upon a pressure gradient defined relative to the distance between heat source and sink. A performance description of say a heat pipe can be adequately represented to this approximation provided the stiffness and compliance coefficients governing behavior are able to react to displacements from steady state in a manner such that the thermodynamic forces governing behavior are maintained at their mean value; that is, a fluctuation must decay as exp(-At). If this is not the case, performance is determined by local conditions, particularly the states of local meniscii. Now, since viscous effects — both transverse and longitudinal — are

responsible for controlling the dissipation of mechanical perturbations at any temperature, it is appropriate that the momentum balance equation serve as a starting point, viz,

$$\partial_t v_i = F_i - P_{ij,\,j}, \tag{1a}$$

with ∂_t and, j serving to specify that a time derivative of the i-th velocity component is to be taken, and a coordinate derivative of the pressure tensor P_{ij}; F_i represents a component of body force. Inertial terms of form $\rho v_j\, v_{i,\,j}$ have been neglected because motion is presumed slow, and between boundaries closely spaced. Taking the variational derivative, multiplying by the velocity variation and integrating over volume elements dV, the result is

$$\frac{1}{2}\partial_t (\delta v_i)^2 = -\delta v_i\, \delta P_{ij}\Big|_1^2 + \int \delta v_{i,\,j}\, \delta P_{ij}\, dV. \tag{2}$$

Incorporating the definition of the pressure tensor

$$P_{ij} = p\,\delta_{ij} + \Pi_{ij}. \tag{3}$$

$$= p\,\delta_{ij} - \frac{1}{2}\eta\,(v_{i,\,j} + v_{j,\,i}), \tag{4}$$

that is, its decomposition into static and viscous parts, the result is

$$\int \frac{1}{2}\partial_t (\delta v_i)^2\, dV = \left\{ \delta v_i\, \delta p_i + \delta v_i \frac{\eta}{2} \delta (v_{i,\,j} + v_{j,\,i}) \right\}\Big|_1^2$$
$$+ \int \delta v_{i,\,i}\ \delta p_i\, dV - \frac{1}{4}\eta \int (\delta v_{i,\,j} + \delta v_{j,\,i})^2\ dV. \tag{5}$$

Under steady state conditions $\delta v_i = O$ at the end points, and $\delta v_{i,\,i} = O$ because the fluid is incompressible at the temperatures in question, and the fluctuation in kinetic energy of the fluid is always damped out by viscous forces:

$$\int \frac{1}{2}\partial_t (\delta v_i)^2\, dV = -\frac{1}{4}\eta \int (\delta v_{i,\,j} + \delta v_{j,\,i})^2\ dV.$$

In the case of tension controlled fluid transport at temperatures where viscosity, surface tension, heat of vaporization, and vapor pressure are varying functions of temperature, δv_i at the meniscii in question need not be zero, and $\delta v_{i,\,i}$ may as a result differ from zero. Under these conditions, stability related to the

behavior of all liquid-vapor-inert gas interfaces in question may effect the bulk liquid in the vicinity of a portion of these interfaces. Considering terms in (5), other than the Rayleigh term, stability or the damping of velocity fluctuations is not apparent unless each of the four terms is considered separately. The first two terms may be written in explicit form:

$$\delta v_i \cdot \delta p_i \Big|_1^2 = \sum_{jK\,i} \int \delta v_i \, \delta p_i \, dA_{jK} \text{ and} \tag{6}$$

$$\delta v_i \frac{\eta}{2} \delta(v_{i,j} + v_{j,i}) \Big|_1^2 \int \delta v_i \, \frac{\eta}{2} \delta(v_{i,j} + v_{j,i}) \, dA_{iK}. \tag{7}$$

Rewriting equation (5) after rearranging such that the terms responsible for instability are to the left of the equals sign and the Rayleigh term to the right of it reads

$$\begin{aligned} &\int \frac{1}{2} \partial_t (\delta v_i)^2 \, dV - \int \delta v_i \cdot \delta p_i \cdot dA_{jK} - \int \delta v_i \frac{\eta}{2} \delta(v_{i,j} + v_{j,i}) \, dA_{iK} \\ &- \int \delta v_{j,i} \cdot \delta p_i \, dV = -\frac{1}{4} \eta \int (\delta v_{i,j} + \delta v_{j,i})^2 \, dV. \end{aligned} \tag{8}$$

The first term is controlled by viscous forces whenever the change of acceleration with time is negative; however, instability sets in if both δv_i and $\partial_t \, \delta v_i$ are negative, that is the flowing mode of the system ceases to function. In referring to the following two terms, it is to be remembered that not only is total area a factor, lets say the areas A_{jK} across which hydrostatic pressures are exerted, but also areas A_{iK} which contain the flow, but also local areal fluctuations. In general for any functional device such as a heat pipe, interfacial area within the system is not a conserved quantity, although total volume is. Observed from this viewpoint, a tension controlled device is a metastable one at best, excepting perhaps a system using a liquid metal where the temperature difference between melting and boiling points is large. Clearly if the aggregated sum of the variational pressure terms in (8) exceeds the Rayleigh term the system is unstable.

Looking into the first of these terms, dA_{ij}, δP_i and δv_i must all be $> O$, if performance is to be increased. For meniscii neighboring a heat source, the

aggregated increase in areas must be small and related to δp_i, which may be defined, e.g.,

$$\delta p_i \begin{cases} = \dfrac{\alpha\gamma}{R_i} - \dfrac{\alpha\gamma}{R_i}\cos\theta_i \\ = -\dfrac{\alpha\gamma}{R_i^2}\,\delta R_i \\ = -\dfrac{\alpha\gamma}{R_i}\sin\theta_i\,\delta\theta_i. \end{cases} \tag{9}$$

the factor, δv_i, simply represents a functional velocity variation for the δp_i given in (9). For the second term, the shear term may be written in the form

$$\begin{aligned} -\eta\,\delta(v_{i,j} + v_{j,i}) &= -\left|\frac{d\gamma}{dT}\right|_o \Delta T \\ &= -\left|\frac{d\gamma}{dT}\right|_o \frac{dT}{dx_j}\,\delta x_j - \left|\frac{d\gamma}{dT}\right|_o \frac{dT}{dx_i}\frac{dx_i}{dS}\,\delta S, \end{aligned} \tag{10}$$

where variations in temperature gradient have been considered relative to the direction of flow, δx_j, and along an element of arc, δS. Both terms in general are greater than zero:

$$\sum_{jK\,i} \int \delta v_i \cdot \delta p_i \cdot dA_{jK} > O, \tag{11}$$

$$\sum \int \delta v_i \frac{\eta}{2}(v_{i,j} + v_{j,i})\,dA_{iK} > O \tag{12}$$

and are destabilizing. This observation may be seen in another manner by considering the Gibbs free energy, G. Because $\delta p_i > O$, there must be an increase in flow work and therefore

$$\delta G > O, \tag{13}$$

that is

$$\delta G = v\delta p + \gamma dA, \tag{14}$$

or

$$N\delta\mu = v\delta p$$

because only isothermal variations are being considered although flow may be taking place above some reference temperature level. But since flow is

continuing with $\delta\theta < O$, then

$$d\mu_i > O \tag{15}$$

and the available energy per particle transferred is increased.

Turning now to a discussion of the third term or dilational factor, we commence from the equation of continuity. At the surface of evaporation, the continuity condition may be written

$$\frac{Q}{h_v} = \rho_L A u, \tag{16}$$

with Q/h_v representing rate of mass transfer based on thermal properties, and $\rho_L A u$ mass transfer rate relative to the fluid properties. Based on the Laplace equation, the surface shape is fixed; once, however, a generalized force such as a thermodynamic force is applied in the neighborhood of a surface, the surface becomes only quasi-fixed, and as a result fits a free surface condition with the initial shape given by the Laplace equation,

$$\overline{\eta} = \eta_0 + \eta_1, \tag{17}$$

but $\overline{\eta} = \overline{\eta}\,(y, t)$ or

$$u = \frac{\partial \overline{\eta}}{\partial t} + v \frac{\partial \overline{\eta}}{\partial y}\ , \tag{18}$$

from (17)

$$u = \frac{\partial \eta_1}{\partial t} + v\left(\frac{\partial \eta_0}{\partial y} + \frac{\partial \eta_1}{\partial y}\right)\ , \tag{19}$$

that is, the particles composing the surface must have a velocity component normal to the flow direction which may or may not coincide with meniscus velocity in that direction. From (16)

$$\frac{\partial (\rho A)}{\partial t} + \nabla (\rho A u) = \nabla\left(\frac{Q}{h_v}\right) \tag{20}$$

but since δv_i are not zero for all interfaces, and points in the bulk liquid, we may write for a surface from (20)

$$\rho_2 A_2 u_2 - \rho_1 A_1 u_1 = \Delta\left(\frac{Q}{h_v}\right) \tag{21}$$

if

$$\frac{\partial (\rho A)}{\partial t} \sim O,$$

and a discontinuity in flow has appeared in the neighborhood of the surface. For simplicity write

$$\rho A (u_2 - u_1) = \Delta \left(\frac{Q}{h_v} \right) \tag{22}$$

or

$$\rho_0 A (u_2 - u_1) - A \left| \left(\frac{d\rho}{dT} \right)_o \right| \Delta T \, u_2 = \Delta \left(\frac{Q}{h_v} \right).$$

If the bulk liquid does not comply then

$$\Delta \left(\frac{Q}{h_v} \right) = \rho_g \, 4\pi R^2 \dot{R} \tag{23}$$

with $u = \mu_2 + \dot{R}$ and a bubble forms. Under circumstances where bulk liquid complies then the equation of continuity for bulk,

$$\frac{\partial (\rho A)}{\partial t} + \nabla (\rho A u) = O \tag{24}$$

or

$$\rho A (u_2 - u_1) \neq O, \tag{25}$$

and

$$\frac{\partial A}{\partial t} \neq O \tag{26}$$

implying that there is an adjustment in area such as a bubble at some point in the bulk liquid not in the immediate vicinity of the meniscus. Whether or not a tension-simulated bubble so formed is a cavitation phenomenon resides in whether or not the process is isothermal. This aspect may be checked from an energy balance in the neighborhood of the bubble:

$$\rho_L \, C_{P_L} \, 4\pi R^2 \Delta \xi \, \Delta T = h_v \, \rho_g \frac{4}{3} \pi R^3 \tag{27}$$

and

$$\Delta \xi = [D \Delta t]^{1/2} \tag{28}$$

with $D = (K/\rho C_{P_L})$ and ρ_g the gas density in the bubble. For water at 15° C the temperature drop amounts to less than a degree (1). The above equation states that the temperature rise due to thermal diffusion from the interface to a distance $\Delta \xi$ in Δt is in this approximation counterbalanced by the vaporization of liquid to a radius R. If ΔT is small then the bubble is produced by tension through competing processes resulting in a small ΔT and cavitation. On the other hand, if ΔT is not small either in a positive or negative direction, the bubble has

been formed by nucleation. In either case the left hand side of (8) may be rewritten,

$$\frac{1}{2}\rho \int \partial_t (\delta v_i)^2 \, dV = \frac{1}{2}\rho \int \partial_t (\delta \dot{R})^2 \, dV, \tag{29}$$

with the volume of integration being taken from the surface of the bubble to all neighboring meniscii for which $\delta p_i \neq 0$.

Ultimately, of course, stability must be related to stiffness coefficients for the working fluid; that is, the derivatives of extensive quantities with respect to intensive ones. Derivatives of intensive quantities with respect to extensive ones serve to define compliance coefficients. The two sets of quantities do not bear a simple reciprocal relationship because different variables are held constant in each definition. The approach taken below is based upon the requirement that the Gibbs free energy be at a minimum.

For the gas and liquid phases to be at minimum free energy, the second variation must satisfy the inequality

$$\delta^2 G > 0 \tag{30}$$

with

$$\delta^2 G = \sum_{i,j} \left(\frac{\partial G}{\partial \xi_i \quad \partial \xi_j} \right)_{\{\xi_K\}, K \neq i,j} \Delta\xi_i \, \Delta\xi_j \tag{31}$$

and $\xi_i = T, P, N, A$, the temperature, pressure, number of particles in the liquid phase, and some interfacial area subject to variation. The conservation relations

$$V_g + V_L = V \tag{32}$$

and

$$N_g + N_L = N \tag{33}$$

hold where g and L refer to gas and liquid phases, respectively. On the other hand interfacial areas are not conserved,

$$0 \leqslant \Sigma \, A_{ijK} \leqslant A_{MAX}. \tag{34}$$

Next (31) is diagonalized by completing the square (2) to give

$$\delta^2 G = \sum_i \lambda_i \zeta_i^2 > 0. \tag{35}$$

the ζ_i do not have physical meaning, but for (35) to be positive definite each λ_i must be greater than zero for all arrangements of terms used as a starting point in completing the square. Results given below are obtained for the ordering: (T, P, N, A). The first two coefficients are

$$\lambda_1 = -\left(\frac{\partial S}{\partial T}\right)_{PNA}$$

$$= -\frac{\partial}{\partial T}\left(\frac{h_v}{T}\right)_{PNA} - 2\frac{\partial}{\partial T}\left(\frac{C_{PL}}{T}\right)_{PNA} + \frac{\partial}{\partial T}\left(\frac{C_{Vv}}{T}\right)_{PNA}; \tag{36}$$

and

$$\lambda_2 = \left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}}; \tag{37}$$

λ_3 and λ_4 are given in the appendix because of their complexity, and not described in detail here. Equation (36) is clearly $> O$ and uninteresting. Relationship (37) on the other hand is interesting so long as

$$\left(\frac{\partial V}{\partial P}\right)_{TNA} > \frac{\left(\frac{\partial V}{\partial T}\right)^2}{\left|\left(\frac{\partial S}{\partial T}\right)_{PNA}\right|} \tag{38}$$

The system is provisionally stable at best, since all possible λ's must be greater than zero for absolute stability. Letting

$$P = \frac{\alpha\gamma}{R}, \tag{39}$$

$$\left(\frac{\partial V}{\partial P}\right)_{TNA} = \left\{\left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial R}{\partial P}\right)\right\}_{TNA}$$

$$= -\left(\frac{\partial V}{\partial R}\right)\left(\frac{\alpha\gamma}{P_C^2}\right) \tag{40}$$

so that

$$\left(\frac{\partial V}{\partial R}\right)_{TNA} < O, \tag{41}$$

where $V = V_L$, liquid volume because $\int V_g\, dP_g \sim O$. To gain some insight into the meaning of this factor, reference is made to Figure 1, which shows the volumes and curvatures in question.

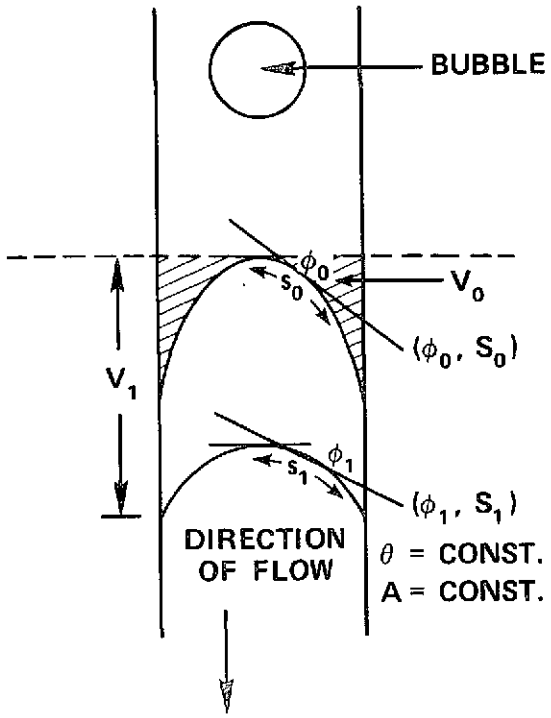

Figure 1. Illustration For λ_2

Referring to Figure 1,

$$\Delta V_L > O,$$

$$dR < O$$

giving

$$\left(\frac{\partial V_L}{\partial R}\right)_{TNA} < O \tag{42}$$

as required for stability. Stability in this case meaning continued flow even though a bubble has formed to conserve area and give momentarily an increase in flow. We are now in a position to reverse the description and explain what has really happened: A temperature has been reached where the meniscus (ϕ_O, S_O) has cavitated liquid nearby because

$$\left|\left(\frac{\partial S}{\partial T}\right)_{PNA}\right|$$

or the vapor pressure (and heat of vaporization) of the liquid is changing more rapidly with temperature than surface tension; hence the meniscus cavitates the

liquid with ϑ = constant in an effort to maintain flow continuity at the liquid vapor interface. What appears as increased performance by bubble-flow stabilization, may eventually, therefore, lead to a break down in flow when the bubble grows to sufficient size to cause the meniscus to revert from state (1) to (0), making

$$\left(\frac{\partial V_L}{\partial R}\right)_{TNA} > 0 \tag{43}$$

and the system unstable.

To lend insight into the order of magnitude of $(\partial V/\partial P)_{TNA}$, a simple calculation is shown for liquid ammonia, writing

$$\left(\frac{\partial V}{\partial T}\right)_{NA} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{NA}$$

and

$$\left(\frac{\partial S}{\partial T}\right)_{PNA} = \frac{1}{T}\frac{\partial h_v}{\partial T} - \frac{1}{T^2} h_v \Delta T \sim \frac{1}{T^2} h_v \Delta T,$$

then at 60° F

$$\frac{1}{\rho^4}\left(\frac{\partial \rho}{\partial T}\right)^2 = 1.17 \times 10^{-9} \text{ (ft}^6/\text{(lb. mass)}^2 \text{ (°F)}^2\text{), and}$$

relative to 0° F

$$\frac{1}{T^2} h_v \Delta T = 1.1 \times 10^{-1} \text{ BTU/(lb. mass) (°R)}^2)$$

giving

$$\left(\frac{\partial(1/\rho)}{\partial P}\right)_{TNA} > 1.06 \times 10^{-8}$$

for stability.

Finally, for situations where a thermal gradient exists between a heat sink and heat source connected by say a fluid artery, the existence of this gradient may serve to alter the boundary conditions determining the flow pattern. Normally, say, for one dimension,

$$\frac{dp}{dx} = \eta \frac{d^2 u}{dy^2} \tag{44}$$

with

$$\frac{du}{dy} = O, \quad y = O \tag{45}$$

and

$$u = O \text{ at the boundaries.} \tag{46}$$

On the other hand, for a tension controlled boundary, the integration constants are obtained from

$$\left(\frac{d\gamma}{dT}\right)_0 \frac{dT}{dy} = \eta \frac{du}{dy} \tag{47}$$

at the boundary, and $\int \rho u dA$ which determines the mass flow rate. Under these conditions it turns out that

$$\left(\frac{du}{dy}\right) = O$$

at the axis, but it may not be used as a condition in view of (47).

Remarks

In a heat pipe, lets say, many interfaces exist: liquid-vapor, liquid-metal, vapor-metal. The liquid-vapor area, in particular, may be characterized by a variety of curvatures. The fact that the liquid-vapor interfacial area is not a conserved, although extended, quantity means that for some range of temperature the thermodynamic and mechanical properties of the liquid can cooperatively remove it from a state of minimum Gibbs free energy, only to be returned by a fluctuation in liquid-vapor interfacial area.

The approach taken in relating the minimization of the free energy to liquid properties does not give a unique solution because diagonalization by completing the square of the polynomial can be carried out in twenty-four ways for the physical situation considered here. Only one such arrangement of terms is considered. However, as can be seen from the discussion of λ_2, at least a portion of the λ factors can be used to suggest experiments for investigating meniscus behavior. The total number of λ's comprises a set of ninety-six. Their determination however, may be easily carried out.

It has been shown also how local meniscus behavior can effect vacinal bubble formation, in particular, formation by cavitation, and how such an event is effected by viscosity.

Extending the notion of stability to rate of entropy production was not undertaken. This approach, however, could be more rigorous. Similarly, looking into the rate of approach of the Gibbs free energy to equilibrium would be useful, since knowing whether or not a fluctuation is damped, or amplified, and under what conditions is important, although not critical for an insight into the motion of stability.

REFERENCES

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APPENDIX

$$\lambda_3 = \left\{ \left(\frac{\partial \mu}{\partial N}\right)_{TPA} - \left(\left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}} \right) \right\} \times$$

$$\frac{\left(\frac{\partial V}{\partial N}\right)^2_{TA}}{\left(\left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}} \right)} - \frac{\left(\frac{\partial \mu}{\partial T}\right)^2_{PA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}}$$

$$\lambda_4 = \left(\frac{\partial \mu}{\partial A}\right)^2_{TP} \left[\frac{1}{\left\{ \left(\frac{\partial \mu}{\partial N}\right)_{TPA} - \left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}} \right\} \frac{\left(\frac{\partial V}{\partial N}\right)_{TA}}{\left(\left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}} \right)} \right]^2$$

$$- \left\{ \left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}} \right\} \frac{\left(\frac{\partial V}{\partial P}\right)^2_{TN}}{\left(\left(\frac{\partial V}{\partial P}\right)_{TNA} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{NA}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}} \right)} - \frac{\left(\frac{\partial V}{\partial T}\right)^2_{PN}}{-\left(\frac{\partial S}{\partial T}\right)_{PNA}}$$